

**UNCLASSIFIED**

**AD 419180**

**DEFENSE DOCUMENTATION CENTER**

**FOR**

**SCIENTIFIC AND TECHNICAL INFORMATION**

**CAMERON STATION, ALEXANDRIA, VIRGINIA**



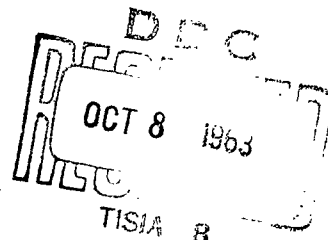
**UNCLASSIFIED**

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

Abstract for International Crystallographic Convention, Leningrad, U. S. S. R.,  
May 21-27, 1959.

Crystal-Structural Mechanism  
of the Ferroelectric Behavior  
of (Glycine)<sub>3</sub>·H<sub>2</sub>SO<sub>4</sub>\*

Ray Pepinsky,  
Department of Physics  
The Pennsylvania State University  
University Park, Pa.,  
and  
Brookhaven National Laboratory  
Upton, Long Island, New York, U. S. A.



Ferroelectric (glycine)<sub>3</sub>·H<sub>2</sub>SO<sub>4</sub><sup>1</sup> crystallizes at room temperature in the monoclinic system with  $a = 9.417$  Å,  $b = 12.643$  Å,  $c = 5.735$  Å,  $\beta = 110^\circ 23'$ ; the space group is  $P2_1$ , and the polar direction is along the two-fold screw axis. Above  $47^\circ\text{C}$  the spontaneous polarization disappears as the space group becomes  $P2_1/m$ . The crystal structure was determined from full three-dimensional x-ray diffraction data, using  $\text{CuK}\alpha$  radiation.<sup>2</sup> Out of the three glycine molecules in the crystal, one has the usual zwitterion configuration, with the  $\text{NH}_3^+$  group out of the plane of the other atoms; the remaining two glycines are mono-protonated, and planar within experimental error, and are designated as glycinium ions. Thus the chemical formula is properly written as  $(\text{NH}_3^+\text{CH}_2\text{COO}^-) \cdot (\text{NH}_3^+\text{CH}_2\text{COOH})_2 \cdot \text{SO}_4^{--}$ , and the compound is best described by the chemical name glycine diglycinium sulfate. One of the planar glycinium ions lies near but not in the plane  $y = 1/4$ , which becomes the mirror plane in the high-temperature phase. There is disorder in this arrangement, even below the Curie point and down to a temperature of  $-70^\circ\text{C}$ .

419180  
419180

\$1.10

The nitrogen atoms form N-H··O hydrogen bonds of the usual strength, whereas a quite strong O-H··O hydrogen bond with a distance of 2.43<sub>8</sub> Å is found between the oxygen atom of the carboxyl group of the zwitter-ion glycine and that of the planar glycinium ion which lies near the plane  $y = 1/2$ . This hydrogen is not in a central potential well; and its shift from one carboxyl group to the other, as the polarization direction is reversed, is accompanied by changes in the stereochemistry of the ions, and by other marked changes in the entire structure. These are described.

Above the Curie point, at 47°C, mirror symmetry is attained by full statistical arrangement of molecules around the mirror planes at  $y = 1/4$  and  $3/4$ .

The structure has been studied by the Okaya-Pepinsky  $P_s(u)$  function,<sup>3</sup> using proportional-counter measurements of scattered CuK $\alpha$  radiation;<sup>4</sup> and the effect of the imaginary part of the sulfur structure factor is sufficient to yield the entire structure. The absolute configuration and direction of structural polarization under an applied electric field is established, therewith.

A neutron analysis<sup>5</sup> has confirmed the x-ray results, and has established the positions of all hydrogen atoms. In particular, the neutron study reveals the non-centered position of the hydrogen between glycine ions near the  $y = 1/2$  plane, and confirms the differences in stereochemistry between the zwitter-ion and monoprotonated glycines.

---

\*Research supported by Air Force Office of Scientific Research, A. R. D. C., Signal Corps Engineering Corps, Office of Naval Research, and U. S. Atomic Energy Commission.

- <sup>1</sup>B. T. Matthias, C. E. Miller and J. P. Remeika, Phys. Rev. 104, 849 (1956).
- <sup>2</sup>S. Hoshino, Y. Okaya and R. Pepinsky, in press, Phys. Rev.
- <sup>3</sup>R. Pepinsky and Y. Okaya, Proc. Nat. Acad. Sci. U. S. 42, 286 (1956).
- <sup>4</sup>F. Unterleitner, Y. Okaya and R. Pepinsky, to be published.
- <sup>5</sup>S. Hoshino, Y. Okaya and R. Pepinsky, to be published.